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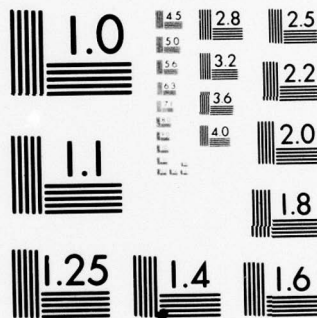
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⑥ RESIDUAL PROTECTIVE LIFE OF CARBON BEDS

⑨ Fifth Quarterly Progress Report, no. 5,

Mar 77 - May 77

by

⑩ Alvin H. Weiss

Thomas Freund

Ehud Biron

⑪ September 1977

⑫ 14p.

WORCESTER POLYTECHNIC INSTITUTE
Department of Chemical Engineering
Worcester, Massachusetts 01609

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experiments are reported which show that the residual life of charcoal filters can be monitored by measuring the chromatographic retention time of a pulse of a probe gas. The retention times of several probe gases were shown to vary with the level of loading of filter-grade charcoals. Pittsburgh ASC and BPL charcoals were used as sorbents, dimethyl methylphosphonate and water as sorbates, and low-molecular-weight hydrocarbons and CO ₂ as probe gases. All experiments were carried out on laboratory-scale beds which simulated.		

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by using beds of the same depth operated at the same linear gas velocity, large-scale breathing-air filters.

The variables investigated included: chemical nature and molecular weight of the probe gas, flow rate, temperature, and geometry of the bed. Laboratory-size scaling of flow rate and bed size can be based on the invariance of the reduced retention time, θ , the retention time divided by the space time. Results of the retention time measurement for residual life are given for the decrease in residual life with a constant DMMP feed level (0.1-mole % in He) flowing into a new filter and with a clean He feed flowing into a partially used filter.

Two basic configurations for measuring the residual life of a filter are suggested, retention time directly on the filter and, second, a simulation mode using a commercial chromatograph. The method depends on the change in retention time per unit weight of charcoal as a function of sorbate loading. The loading-retention time dependence is associated with the change in the isotherm of the probe gas as a function of sorbate loading.

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PREFACE

The work described in this report was authorized under Contract No. DAAA 15-76-C-0072, "Residual Protective Life of Carbon Beds". The work described covers the period of March 1 to May 31, 1977.

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RESIDUAL PROTECTIVE LIFE OF CARBON BEDS

I INTRODUCTION

This fifth quarterly report, covering the period 1 March 1977 to 31 May 1977, is arranged in three parts:

- I Introduction
- II Summary of Results of Experiments Designed to Simulate the Decrease in Residual Life Following an Attack and the Movement of Adsorbed DMMP Through a Carbon Bed
- III Suggestions for Future Work

Part I is based on details to be found in the first four quarterly reports with the exception of: retention time studies using water as a sorbate, retention time as a function of the diameter of the bed, retention time as a function of flow rate for a bed of the same length as the large scale filter, i.e., one inch.

The objective of this contract is to find a non-destructive test of the residual life of charcoal filter that is used to purify breathing air for occupants of a building in the case of a war-gas attack. The non-destructive test is simply measuring the retention time of a pulse of a probe gas. A simple correlation was found between the retention time of several probe gases and the loading of charcoal beds with dimethyl methylphosphonate (DMMP), a nerve gas simulant.

II RESIDUAL LIFE AFTER A GAS ATTACK

The complex situation of the residual life and its measurement was considered for the situation of clean air traveling through a filter after a gas attack. This situation was simulated by making up beds from two sections connected in series with the section at the inlet end presaturated with DMMP and the outlet section free of DMMP. A feed stream of DMMP-free He was used instead of clean air. Periodically the retention time of a probe gas was measured on the total bed and the weight of each section was determined to measure the amount of sorbed DMMP. At the end of the experiment the retention time of each section was determined. The experiments were carried out on two beds of the same total length. Bed A was prepared with a presaturated section one third of the total length of the bed; Bed B with a presaturated section two-thirds of the total length. Tables 1 and 2 summarize the results obtained.

With increasing time of flow of DMMP-free He, the retention time on the total bed decreased as DMMP was desorbed from the inlet section and sorbed on the outlet section. At the longest times of flow for Bed B, breakthrough of DMMP occurred from the initially DMMP-free outlet section.

From the retention time measurements at the end of the experiments (about 50% of the DMMP was transferred from the inlet to the outlet sections) on each section it was found that the decrease in retention time of the total bed is associated with a large decrease in the retention time of the initially DMMP-free outlet section while the increase in retention time of the inlet section was small. This finding is consistent with the result that the retention time

TABLE 1

RETENTION TIME AS A FUNCTION OF DMMP DISTRIBUTION

2.00g ASC Carbon Flow rate ~80cc/min Column 3-3' 2-2' Test Gas 0.25cc CO₂
 Temperature 29-30°C Column 3-3' = 0.6673g ASC Carbon, Column 2-2' = 1.3307g

Time of Gas Flow (hrs)	vol. of Gas Flow l	3-3'	2-2'	Total	Flow rate cc/min	Ret. time min	$\frac{Ft}{V}$ s	$\frac{wt\ 2-2'}{wt\ 3-3'} \times 100$
0	0	0.2251	0.0000	0.2251				
0.68	3.1	0.2141	0.0115	0.2256	75.9	2.73	50.8	5.4
1.00	4.5	0.2090	0.0169	0.2259	75.9	2.70	50.2	8.09
7.30	34.8	0.1807	0.0478	0.2285	81.2	2.10	41.8	26.5
7.55	36.3	0.1796	0.0488	0.2283	81.2	2.10	41.8	27.2
10.00	47.5	0.1727	0.0580	0.2307	75.7	2.03	37.7	33.6
10.20	48.4	0.1721	0.0588	0.2309	75.7	2.05	38.0	34.2
78.8	380	0.1377	0.0871	0.2248	80.5	1.95	38.5	63.6
78.8	380	0.1377	0.0871	0.2248	80.5	1.88	37.1	63.6
103.6	492	0.1318	0.0888	0.2206	75.4	1.98	36.6	67.4
249.3	717	0.1105	0.1082	0.2187	79.8	1.90	37.2	97.9
249.3	717	0.1105	0.1082	0.2187	79.8	1.92	37.6	97.9
344.2	1289	0.0993	0.1103	0.2096	74.8	1.75	32.1	111
513.6	2158	(0.0891)	(0.1214)	(0.2105)	85.5	1.51	31.6	(136)
611.9	2648	0.0910	0.1122	0.2032	92.9	1.41	32.1	123

TABLE 2

RETENTION TIME AS A FUNCTION OF DMMP DISTRIBUTION

2.00g ASC Carbon; Flow Rate 80cc/min; Column 1-1'/4-4'; Test Gas: 0.25cc CO₂;
 Temperature: 29-30°C; Column 1-1' : 1.3288g ASC Carbon, Column 4-4' : 0.6678g

Time of Gas Flow (hrs)	Vol of Gas Flowed (l)	1-1'	4-4'	total	Flow rate (cc/min)	Ret. time (min)	$\frac{F_t}{V_s}$	$\frac{\text{wt 4-4'}}{\text{wt 1-1'}} \times 100$
0	0	0.4425	0.0000	0.4425				
0.62	2.9	0.4298	0.0124	0.4422	80.5	1.35	26.6	2.8
0.90	4.3	0.4240	0.0181	0.4421	80.5	1.33	26.2	4.1
7.42	35.5	0.3727	0.0686	0.4413	79.9	0.91	17.8	16.4
7.67	36.7	0.3716	0.0695	0.4411	79.9	0.89	17.4	18.7
9.75	47.2	0.3614	0.0774	0.4388	77.4	0.90	17.1	21.4
9.93	48.0	0.3606	0.0781	0.4386	77.4	0.91	17.3	21.7
78.8	372	0.2878	0.1436	0.4314	78.1	0.78	14.9	49.9
78.8	372	0.2878	0.1436	0.4314	78.1	0.76	14.5	49.9
103.6	486	0.2766	0.1496	0.4262	77.0	0.68	12.8	54.1
249.3	1160	0.2367	0.1644	0.4251	78.1	0.63	12.1	69.5
249.3	1160	0.2367	0.1644	0.4251	78.1	0.65	12.4	69.5
344.2	1582	0.2167	0.1528	0.3695	73.8	0.73	13.2	70.5
513.6	2420	0.1945	0.1431	0.3376	82.4	0.74	14.9	73.6
611.9	2907	0.1980	0.1330	0.3310	90.9	0.71	15.8	67.1

$V_s = 4.08\text{cc}$

is constant and very short above a homogeneous loading of about 0.1g DMMP/g charcoal. Therefore, the inlet section loses DMMP without much change in retention time because most of the section contains DMMP above a loading level of 0.1g/g charcoal. In contrast the outlet section gains DMMP with a decrease in retention time.

The weight loss of DMMP from each inlet section, as a function of time of flow of DMMP-free He feed, followed the rate law:

$$wt_{DMMP} = c \log (t + t_0)$$

where c and t_0 are fitting constants. The weight loss rate was proportional to the length of the initially saturated section indicating that DMMP was removed by the vapor phase over the whole length of the inlet section.

The significance of these experiments is (1) the residual protection life of a filter continues to decrease after an attack while clean air is flowing through the filter (2) this decrease in residual life is reflected in a decrease of the retention time of the probe gas. A filter should be discarded after any attack, because eventually the sorbed new gas will migrate and "breakthrough".

III SUGGESTED AREAS FOR FUTURE WORK

1. Effect of Other Sorbates on Retention Time of Probe Gas: While we have carried out retention time experiments with a variety of probe gases as a function of DMMP loading and with one probe gas at one water loading, it cannot be concluded with certainty that the retention time is a function only of the loading level and independent of the chemical nature of the loading substance (sorbate). We believe it may be desirable to find a probe gas that would show selectivity with respect to the chemical nature of the sorbate for several practical reasons given in the following paragraph.

First, it would be desirable to have information from the retention time concerning the nature of the sorbate to identify if a poison gas attack is or has occurred. Second, it is expected that some sorbates will displace other sorbates from charcoal. For example, loading with water may not materially decrease the residual loading capacity for DMMP.

Let us speculate about a specific situation to make the problem clearer. Suppose the feed stock is composed of DMMP (the nerve gas simulant) at P/P_0 about 0.1 and H_2O at P/P_0 about 0.8, a mole ratio of H_2O to DMMP of 300. After a time we would expect that a small length of the charcoal at the inlet end would be loaded with DMMP; downstream from the DMMP loaded section, the charcoal would be loaded with H_2O . With respect to the effluent from the bed, no breakthrough for DMMP has occurred but breakthrough for water has occurred. If the loading has occurred in this manner, we believe that ethane, as a probe gas, would not distinguish this situation from a bed completely loaded with DMMP.

It is essential to know the behavior of a bed with multiple component feeds.

We suggest that it may be possible to find a probe gas which has sorption constants of the same magnitude for bare charcoal and H_2O covered charcoal. If such a probe gas can be found, the retention time of this probe gas would be independent of water loading.

It should be pointed out, because of the "S" shape of the water isotherm on charcoal, that the water loading of charcoal should be negligible with a feed stock containing less than P/P_0 of 0.4 (40% R.H.). Thus, at lower humidity, ethane can be expected to be a suitable probe gas to measure the residual capacity of the bed for DMMP. An experiment should be carried out establishing this expectation.

2. Size of Probe Gas Sample: While we have shown that there is an effect of sample size of the probe gas on retention time, a simple relationship exists between retention time and loading at constant sample size for a given geometry of the charcoal bed.

We suggest that the retention time be studied as a function of the ratio of the probe gas sample size to diameter of the charcoal column.

For maximum sensitivity of the retention time with loading we believe that instead of injecting the pure probe gas it would be better to inject a sample of the probe gas diluted by the carrier gas, i.e., air or nitrogen. This belief is based on the dependence of the retention time on the shape of an isotherm. In general, the retention time increases with increasing steepness of the isotherm, i.e., dq/dp where q is the amount sorbed and p is the partial pressure of the sorbate, and the value of dq/dp usually increases with decreasing p until a constant maximum value. Therefore, it is desirable to use the probe gas at low partial pressures so that the retention time is maximized. It should be noted that this effect is particularly important on short columns with short retention times since in this situation the partial pressure does not decrease very much as the pulse travels through the column. The term "linear chromatography" is applied to the situation where the partial pressure is low enough so that the isotherm is linear, i.e., q is a linear function of p .

The lower limitation of the partial pressure of the probe gas in the injected sample is given by the sensitivity of the detector.

3. Diameter Scale Up: While a scale up of 50% in the 1/4 inch diameter range was shown to have no effect, it is suggested that a much wider range is needed since the filters are on the order of several feet linear cross section.

4. Desorption and Migration of DMMP in a Charcoal Column: While we have carried out desorption and migration experiments, the results were based on weight changes of the charcoal columns. We believe these results should be confirmed by chemical analyses of the charcoal and the effluent streams for DMMP.

The charcoal, we believe, can be analyzed for the quantity of adsorbed DMMP by extraction of the charcoal with a volatile solvent such as acetone or ether and analyzed by gas-liquid chromatography. We suggest that an 1/8 inch

diameter 12 foot long column of 15% silicone DC LSX 3-0295 on 40-60 mesh Chromosorb T operated in the range of 140° to 170° should be suitable at a flow of 20 to 40 cc/min. The volatile solvent should elute first. For most sorbed DMMP determinations, the thermal conductivity detectors should be satisfactory since analysis at the 25 µg and up range was found to be feasible. Flame ionization is preferable for effluent gas analysis since the amounts of DMMP are much lower.

5. Literature Search and Theoretical Treatment: A literature search will be completed in order to:

- a) find a candidate substance which will have a large sorption on DMMP covered charcoal and negligible sorption on bare charcoal
- b) find a candidate heterogeneously catalyzed reaction whose rate varies with DMMP loading. Low temperature reactions such as PARA-ORTHO hydrogen conversion will be considered
- c) find principles which may govern the retention time as a function of the chemical nature of the impurity sorbate
- d) find the principles that govern the migration of sorbed DMMP toward the downstream end of a bed
- e) utilize the background existing in modified GSC to tailor probe gases to specific situations and to develop a more general scientific basis for residual life estimation.
- f) key words for computerized search:

Adsorption

by charcoal
carbon
filters
gas mask

Adsorption gas chromatography
isotherm
constant

Adsorbent

Canister

Carbosieve

Charcoal

Filter

Gas Mask

Residual life

Gas chromatography

separation by
loading (of column)
tailing
retention time
retention volume

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